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Technical Progress Report on Single Pass Flow Through Tests of Ceramic Waste Forms for Plutonium Immobilization

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December 3, 2000

U.S. Department of Energy

Lawrence
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DISCLAIMER

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INTRODUCTION

This report updates work on measurements of the dissolution rates of single-phase and multi-phase ceramic waste forms in flow-through reactors at Lawrence Livermore National Laboratory. Previous results were reported in Bourcier (1999)*.

Two types of tests are in progress: (1) tests of baseline pyrochlore-based multiphase ceramics; and (2) tests of single-phase pyrochlore, zirconolite, and brannerite (the three phases that will contain most of the actinides). Tests of the multi-phase material are all being run at 25°C. The single-phase tests are being run at 25°, 50°, and 75°C. All tests are being performed at ambient pressure. The as-made bulk compositions of the ceramics are given in Table 1.

The single pass flow-through test procedure [Knauss, 1986 #140] allows the powdered ceramic to react with pH buffer solutions traveling upward vertically through the powder. Gentle rocking during the course of the experiment keeps the powder suspended and avoids clumping, and allows the system to behave as a continuously stirred reactor. For each test, a cell is loaded with approximately one gram of the appropriate size fraction of powdered ceramic and reacted with a buffer solution of the desired pH. The buffer solution compositions are given in Table 2.

All the ceramics tested were cold pressed and sintered at 1350°C in air, except brannerite, which was sintered at 1350°C in a CO/CO_2 gas mixture. They were then crushed, sieved, rinsed repeatedly in alcohol and distilled water, and the desired particle size fraction collected for the single pass flow-through tests (SPFT). The surface area of the ceramics measured by BET ranged from 0.1 - 0.35 m^2/g. The measured surface area values, average particle size, and sample weights for each ceramic test are given in the Appendices.

* Bourcier, W. L. (1999). Interim report on development of a model to predict dissolution behavior of the titanate waste form in a repository and compilation of data from SPFT ceramic dissolution tests (FY99 milestones 4.1e and 4.1f), Lawrence Livermore National Laboratory, UCRL-ID-135363, PIP-00-003. 55 p.

Table 1. Compositions of ceramics used in SPFT dissolution tests.

		P104				Impure Feed (Batch 4)			
Oxide	Element	Oxide		Element		Oxide		Element	
		wt%	mole%	wt%	mole%	wt%	mole%	wt%	mole%
	O	--	--	25.1	63.6	--	--	24.1	63.8
CaO	Ca	12.6	25.0	9.0	9.1	9.9	21.2	7.1	7.5
UO2	U	30.2	12.5	26.7	4.5	23.6	10.5	20.8	3.7
PuO2	Pu	--	--	--	--	11.9	5.2	10.5	1.8
CeO2	Ce	9.6	6.3	7.8	2.3	--	--	--	--
Gd2O3	Gd	--	--	--	--	7.9	2.6	6.9	1.8
TiO2	Ti	35.8	50.0	21.4	18.2	35.9	54.1	21.5	19.0
HfO2	Hf	11.8	6.3	10.0	2.3	10.6	6.1	9.0	2.1
Ga2O3	Ga	--	--	--	--	0.14	0.09	0.10	0.06
ZnO	Zn	--	--	--	--	0.11	0.14	0.07	0.05
MgO	Mg	--	--	--	--	0.02	0.06	0.01	0.02
		P139 (zirconolite ceramic)				P137 (pyrochlore ceramic)			
Oxide	Element	Oxide		Element		Oxide		Element	
		wt%	mole%	wt%	mole%	wt%	mole%	wt%	mole%
	O			24.9	64.0	--	--	24.9	63.8
CaO	Ca	9.7	20.2	6.9	7.1	10.5	21.7	7.5	7.7
UO2	U	16.1	7.0	14.2	2.5	24.3	10.4	21.4	3.7
PuO2	Pu	--	--	--	--	--	--	--	--
CeO2	Ce	6.4	4.3	5.2	1.5	8.4	5.7	6.9	2.0
Gd2O3	Gd	6.9	2.2	6.0	1.6	8.1	2.6	7.1	1.8
TiO2	Ti	35.5	52.1	21.3	18.3	36.2	52.7	21.7	18.6
HfO2	Hf	25.4	14.1	21.5	5.0	12.5	6.9	10.6	2.4
Ga2O3	Ga	--	--	--	--	--	--	--	--
ZnO	Zn	--	--	--	--	--	--	--	--
MgO	Mg	--	--	--	--	--	--	--	--
		Brannerite							
Oxide	Element	Oxide		Element					
		wt%	mole%	wt%	mole%				
	O	--	--	22.8	66.7				
UO2	U	61.1	31.7	53.9	10.6				
TiO2	Ti	38.9	68.3	23.3	22.8				

The flow-through tests were run at various flow rates ranging from 10 to 100 ml/day. The flow rates for each test are given in the Appendices. Peristaltic pumps were used to control flow rate. A debubbler cell was placed in line for each buffer solution. The debubbler allows the gas exsolved during heating of the fluid to escape, avoiding the capture of bubbles inside the reaction chamber.

Table 2. Buffer solution compositions.

pH	Buffer Components	Concentration
pH 2	HCl	0.01 molal
pH 4	Potassium acid phthalate-HCl	0.001 molal
pH6	Potassium acid phthalate-NaOH	0.001 molal
pH8	Boric acid-NaOH	0.005 molal
pH 8.5	$NaHCO_3$	0.005 molal
pH10	Boric acid-NaOH	0.005 molal
pH12	NaOH	0.01 molal
pH12	Na_2CO_3-NaOH	0.01 molal
pH12	K_2HPO_4-NaOH	0.01 molal

The reacted solutions were periodically sampled, weighed to determine flow rates, and analyzed by ICP/MS for cerium, gadolinium, hafnium, titanium, and uranium. The concentration data were used to compute the normalized release rate, which is defined as:

$$NR_i = \frac{C_i * Q}{S * m * X_i}$$

where C_i is the blank-corrected concentration of element i in the buffered leach solution (per unit volume), Q is the solution flow rate, S is the BET-measured specific surface area of the ceramic, m is the mass of ceramic, and X_i is the weight fraction of element i in the ceramic. Normalized release rates in units of $g/m^2/day$ for each element are given in the Appendices.

SUMMARY OF DATA

Tests of the U-Pu multi-phase pyrochlore-based ceramic waste form

The SPFT tests of the plutonium-bearing pyrochlore-based ceramic were carried out in pH buffers of 2, 4 and 6 at room temperature. The tests have been ongoing for 34 months. Figure 1 shows the dissolution rates of Pu and U as a function of time at the three pH values tested. Release rates are highest at low pH. At a given time and pH, the normalized release rates for U and Pu are approximately the same. The release rates decrease with time, and the effect of pH tends to decrease with time.

Figure 2 compares the dissolution rates of all the elements (except Ca) in the U-Pu ceramic at each pH tested. The elemental release becomes more non-stoichiometric as the solution pH increases from 2 to 6. However, even at pH 6, elemental releases become more congruent with time. The concentrations of some elements such as Hf and Ti in pH 6 leachate are near or below the detection limits of ICP-MS. The amounts of Ca released from the ceramic were below background because of the high background levels of Ca under standard laboratory conditions.

Tests of the U-Ce multi-phase pyrochlore-based ceramic waste form

Two sets of room temperature SPFT tests of the U-Ce ceramic are in progress; tests at pH 2, 4, 6, and 8; and tests at pH 9, 10 and 12. Ce serves as an analog for Pu in these ceramics. Because the ceramic contains no Pu the tests do not need to be performed in a glovebox. The pH 2-8 tests have been ongoing for 35 months. The pH 9-12 tests have been ongoing for 28 months. Figure 3 shows the normalized release rates for elements in the U-Ce pyrochlore ceramic waste form as a function of time. The data trends are consistent with those obtained from the tests of U-Pu ceramic samples. The normalized release rates of uranium at pH 2 to 9 clearly continued to decrease for the duration of the

tests; however, the release rates at higher pHs seem to have leveled off between 1.5 and 2 years. Note that although Ce and U are released congruently at low pH values (Figure 3), at pH 8 and higher, U is released faster than Ce. This probably is due to a lower relative solubility of Ce vs. U at neutral to alkaline pH values.

At pH 12, three different buffers were used to study the effects of various anions (hydroxide, carbonate, and phosphate) on dissolution behavior. After a year of reaction, uranium release rates started showing a dependence on solution composition (see Figure 4a). The release rate of uranium in these buffers decreases in the order: Na_2CO_3 > NaOH > K_2HPO_4. The anion species apparently participate in the reactions controlling the release of U. However, Ti and Hf do not appear to be affected by the anion present, at the resolution of our tests (Figures 4b and 4c).

Two more SPFT tests (at pH 2 & 4) for the multiphase ceramic BSL8 (received from PNNL) at room temperature were started in February 2000. An earlier sample of this formulation tested at PNNL showed anomalous release rate data; normalized release rates for some elements increased with time. No analytical data are currently available from our tests on this material. Data on this test will be reported in the next data update.

Tests of U-Ce single-phase ceramics

SPFT tests on nominally single-phase pyrochlore[1] ($(Ca,Gd)(Hf,Ce,U,Gd)Ti_2O_6$), zirconolite ($(Ca,Gd)(Hf,Ce,U,Gd)Ti_2O_6$), and brannerite ($UTi_2O_6$) ceramics are being carried out at 25°, 50° and 75 °C over a pH range of 2-12. The tests of the pyrochlore and zirconolite have been in progress for 24 months. The tests of the brannerite have been in progress for 15 months. They are all currently being maintained at 75°C with infrequent sampling. It should be noted that these ceramics all contain small amounts of rutile and

[2] Although pyrochlore and zirconolite have the same chemical formula, the pyrochlore contains greater amounts of U and Ce and a lesser amount of Hf than zirconolite (see Table 1) and because of this crystallizes with a different structure.

mixed Ti-Hf oxides (<10 volume %). The pyrochlore ceramic also contains a small amount of brannerite (<2 volume %). The presence of small amounts of other phases may affect the interpretation of the data.

Figures 5 to 7 show normalized uranium release rates observed in each phase at 25°, 50° and 75°C, respectively. Only uranium data are plotted. Uranium was generally above detection limits at all pH values and therefore shows the best trends. Other elements were detectable only under a subset of test conditions. The concentrations of all analyzed elements are given in Appendix C, D and E. In general, the highest release rates are obtained for brannerite with rates of $10^{-3} - 10^{-4}$ g/m^2/day obtained at the longest durations. Rates for pyrochlore and brannerite are typically an order of magnitude lower at similar pH and temperature.

The data show a progressive increase in non-stoichiometry of release as the pH increases from 2 to 10. At pH 2, Ca, U, Ce, and Ti are all released at nearly the same rate. At higher pH values, elements other than U leach at slower rates. Most of the data show a continuous decrease in release rate with time, similar to the Pu-U ceramic release rate data.

Summary of dissolution rates as function of pH

Figure 8 compares normalized release rates of uranium for both single phase and multi-phase ceramics as a function of pH at room temperature. The data are averages of measured values over the 90 to 120 day sampling period for all the ceramics except brannerite, for which the 19-26 day data were used. The error bars represent one standard deviation on the average of the analytical data. The curves show a general trend of decreasing dissolution rate with pH up to near neutral pH, with perhaps a minimum at neutral pH, and little or no effect of pH at higher pH values. The single phase zirconolite and pyrochlore ceramics are slightly more durable than the multiphase ceramics. The

single phase brannerite is about two orders of magnitude less durable than the other single phase ceramics and the multi-phase ceramics. The multi-phase ceramics probably show higher release rates because they contain some of the less durable brannerite phase.

Figure 9 compares beginning and ending normalized release rates for uranium from multi-phase ceramics as a function of pH. With time, the release rates slow down, as noted previously. However, the Ce-U ceramic release rate slows down more than the Pu-U ceramic release rate. This is better seen in Figure 10 where the ratio of the normalized release rate of U from the Pu-U ceramic over the normalized release rate of U from the Ce-U ceramic is shown as a function of time. A positive slope of the data indicate the durability of the Ce-U ceramic increases with time relative to the Pu-U ceramic. The implication is that the data may be showing radiation damage due to alpha decay of Pu in the Pu-U ceramic that is not be present in the Ce-U ceramic. A preliminary calculation indicates that something near ten to the twentieth atoms per cm^3 would have been displaced from their lattice sites by reason of the alpha decay by during the three year test duration (Rich Van konynenburg, pers. com.). There are a few times ten to the twenty-first atoms per cm^3 for this high material, so a couple % the atoms may have been displaced. Whether this trend is real and whether radiation damage is the cause cannot be determined with a high degree of certainty given the uncertainty of these data.

CONCLUSIONS

Some generalizations can be made based on these test results. The normalized release rates for most elements continue to decrease with time, although for some materials and pH conditions, they appear to be at or near steady state (after 3 years). There appear to be no cases where the release rates accelerate dramatically as has been observed in multi-year tests of silicate glasses. At low pH values, Hf is released more slowly and Gd at about the same rate as Pu. At neutral to alkaline pH values, all of these elements are released at

rates so slow that analytical limitations make it difficult to determine relative release rates with much certainty.

The single phase tests consistently show that brannerite is the least durable phase, by 1-2 log units. Zirconolite and pyrochlore appear to be comparable in durability, especially when a correction is made for the small amount of brannerite present in the pyrochlore material.

With time, the effect of pH on dissolution rate becomes less pronounced, except perhaps for the single phase brannerite.

And finally, in tests at pH 12 with three different anions present (hydroxide, carbonate, and phosphate), carbonate appears to enhance the dissolution rate relative to simple hydroxide, and phosphate decreases the rate relative to simple hydroxide. But the overall effect of the anions is a factor of 10 or less.

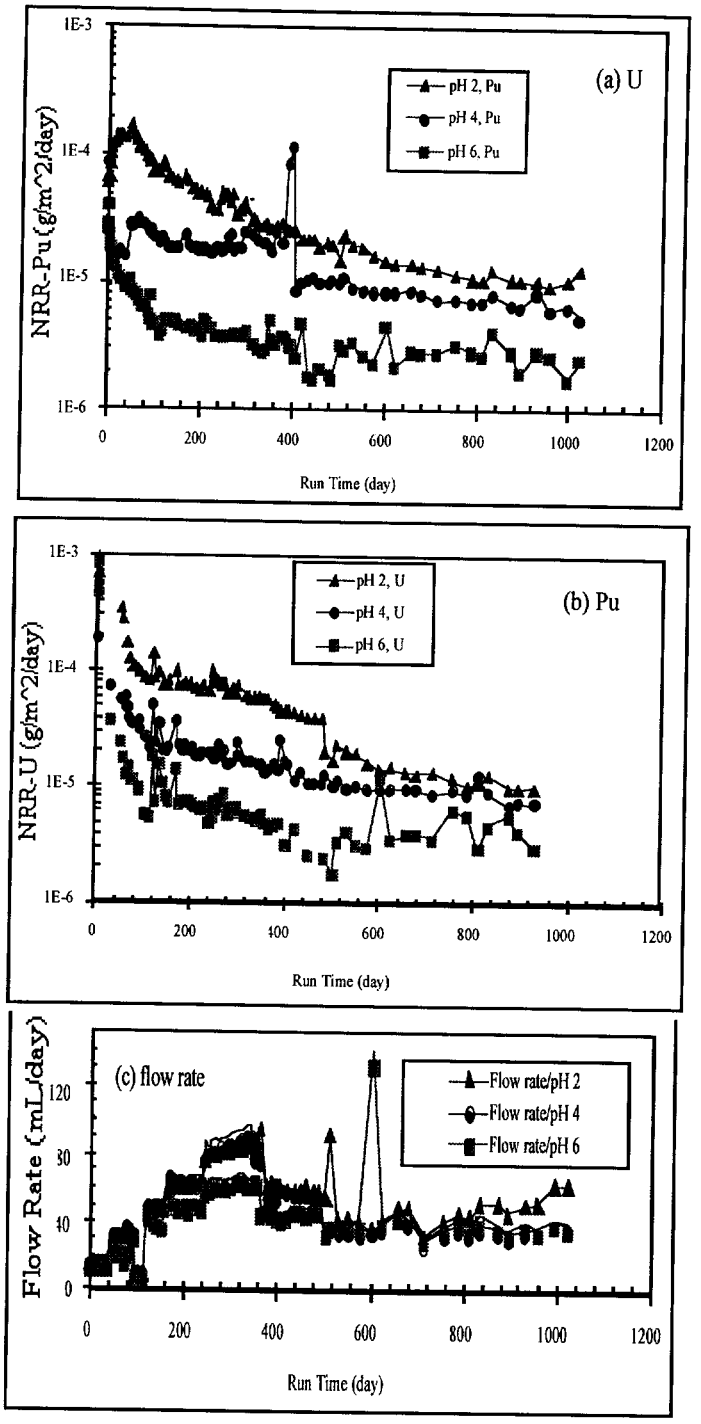

Figure 1. Normalized release rates of elements from the U-Pu multi-phase pyrochlore –based ceramic waste form (Impure Feed, batch 4). (a) normalized release rate of Pu, (b) normalized release rate of U, and (c) flow rates.

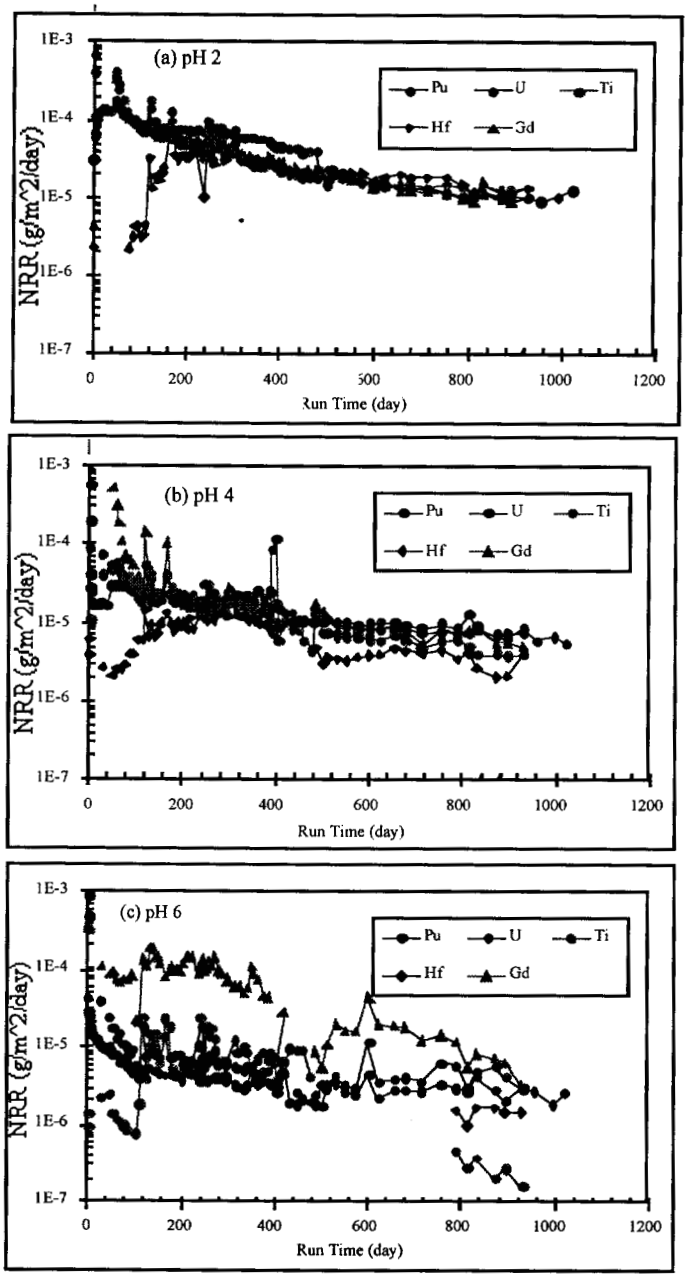

Figure 2. Normalized release rates of plutonium, uranium, titanium, hafnium and gadolinium in U-Pu multi-phase pyrochlore ceramic waste form (Impure Feed, batch 4) at pH (a) 2, (b) 4, and (c) 6

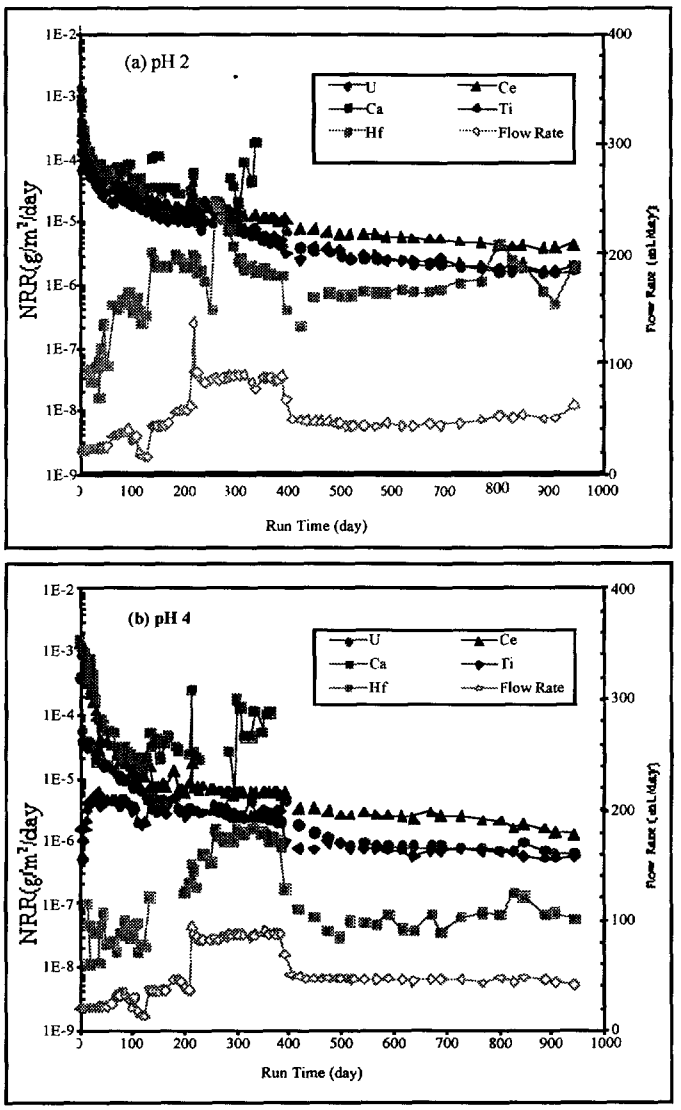

Figure 3. Normalized release rates of major elements in U-Ce multi-phase pyrochlore ceramic waste form (P104) and flow rates at pH (a) 2, (b) 4.

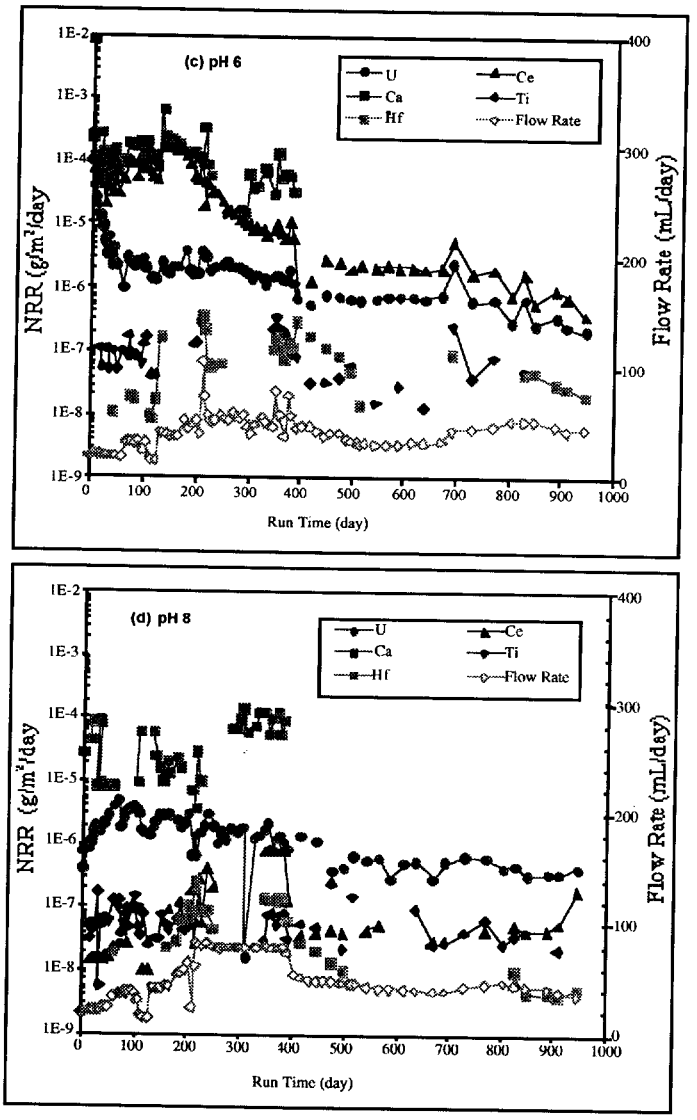

Figure 3 (cont). Normalized release rates of major elements in U-Ce multi-phase pyrochlore ceramic waste form (P104) and flow rates at pH (c) 6, (d) 8.

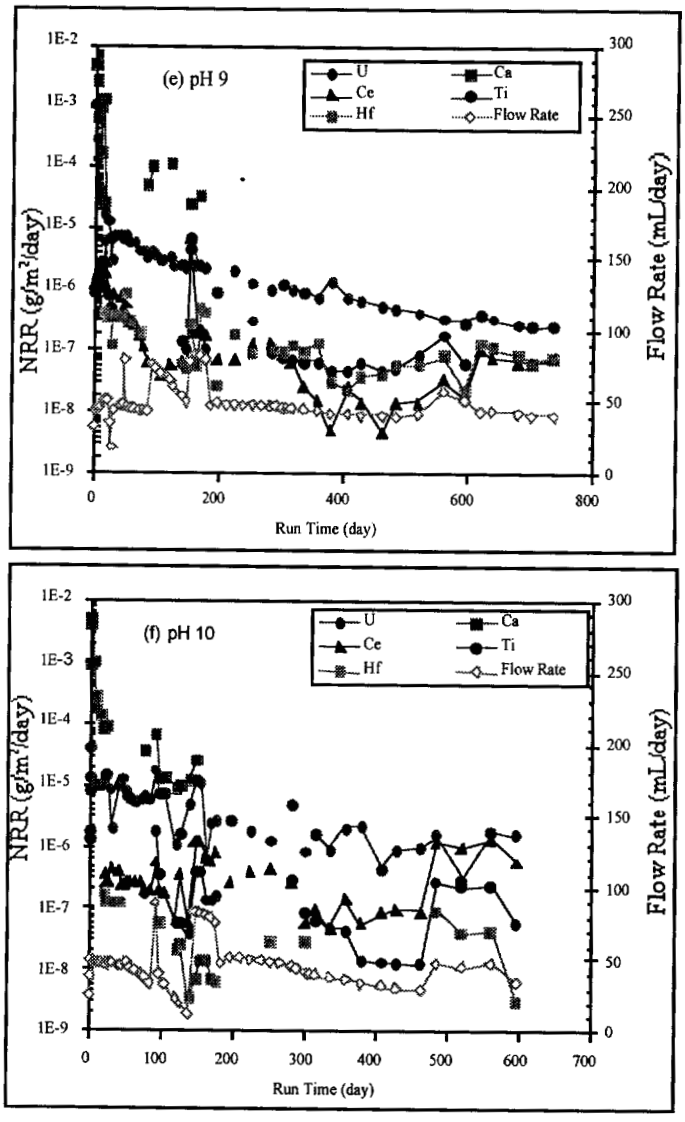

Figure 3 (cont). Normalized release rates of major elements in U-Ce multi-phase pyrochlore ceramic waste form (P104) and flow rates at pH (e) 9, (f) 10.

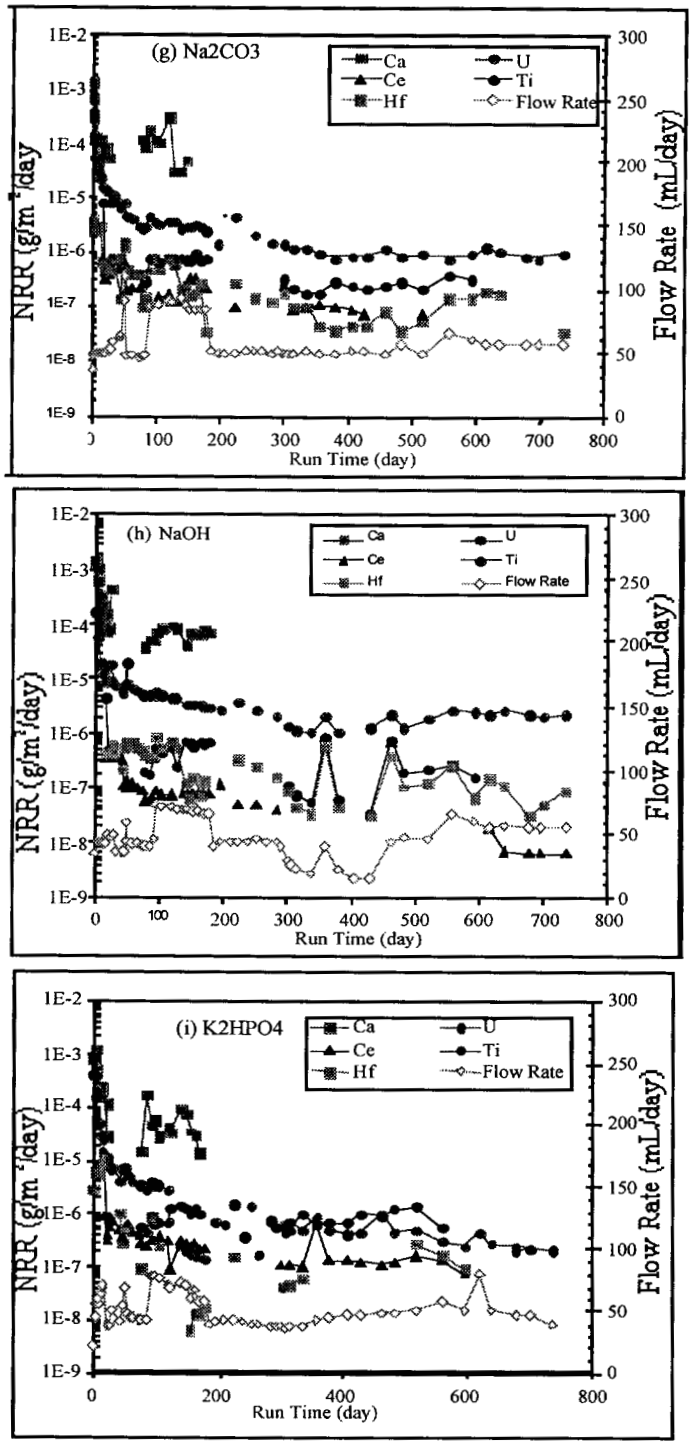

Figure 3 (cont). Normalized release rates of major elements in U-Ce multi-phase pyrochlore ceramic waste form (P104) and flow rates in three different buffers (g) Na_2CO_3, (h) NaOH, and (i) K_2HPO_4) at pH 12.

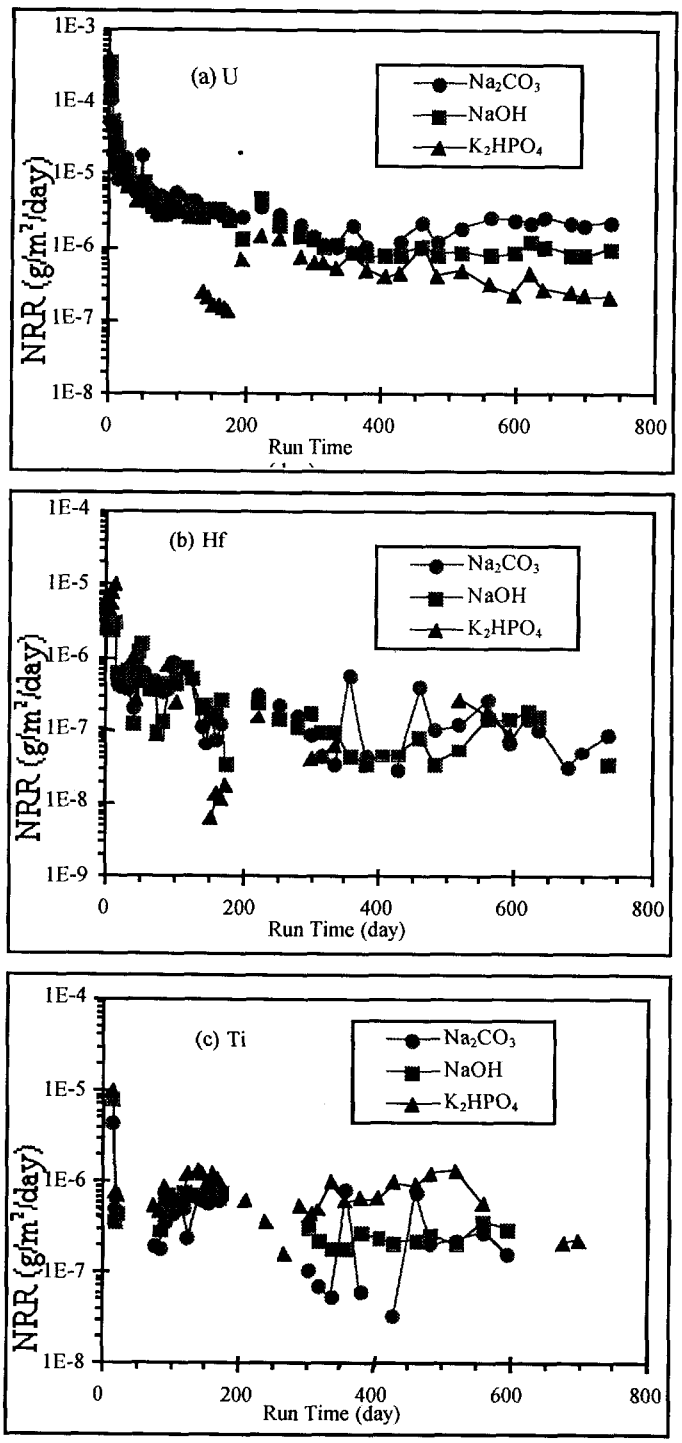

Figure 4. Effects of pH buffer chemistry on the dissolution rates of (a) U, (b) Hf and (c) Ti in U-Ce multi-phase pyrochlore-based ceramic waste form at pH 12.

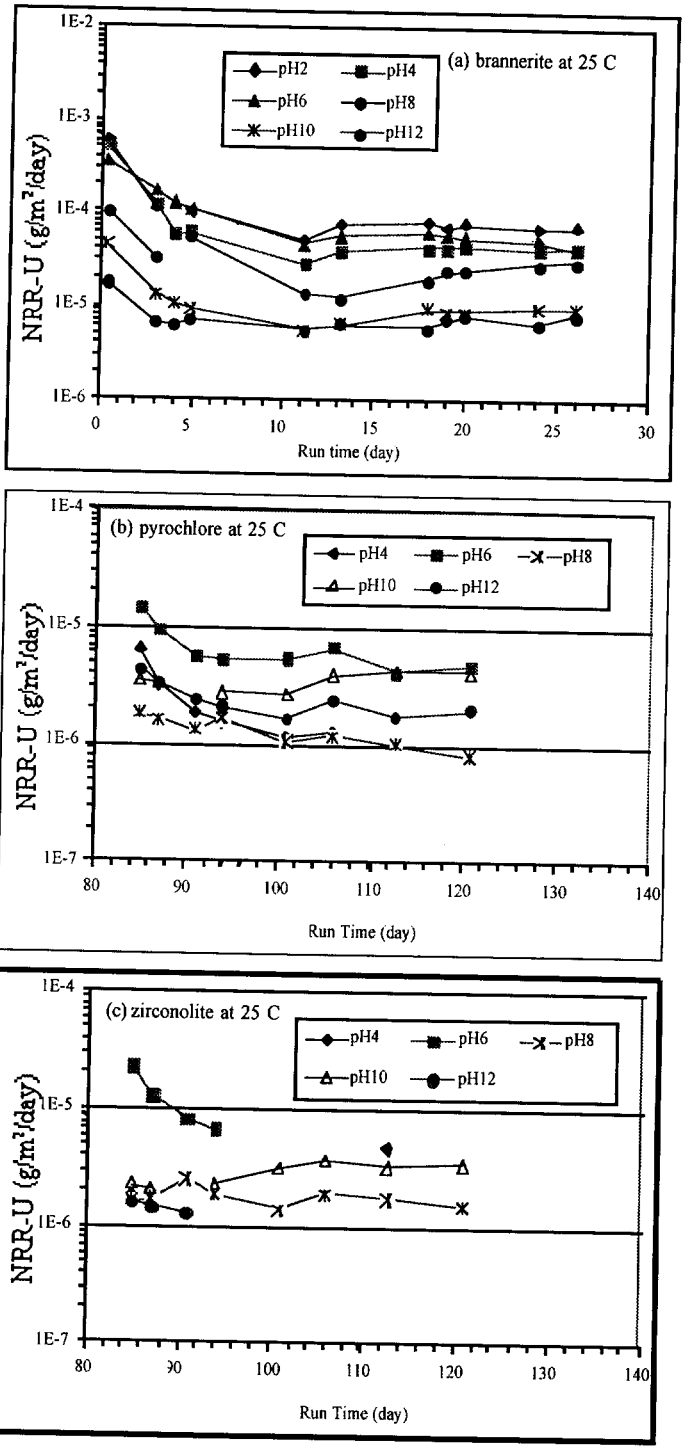

Figure 5. Normalized release rates of uranium from single-phase ceramics at 25° C for (a) brannerite, (b) pyrochlore, and (c) zirconolite. As-batched bulk compositions given in Table 1.

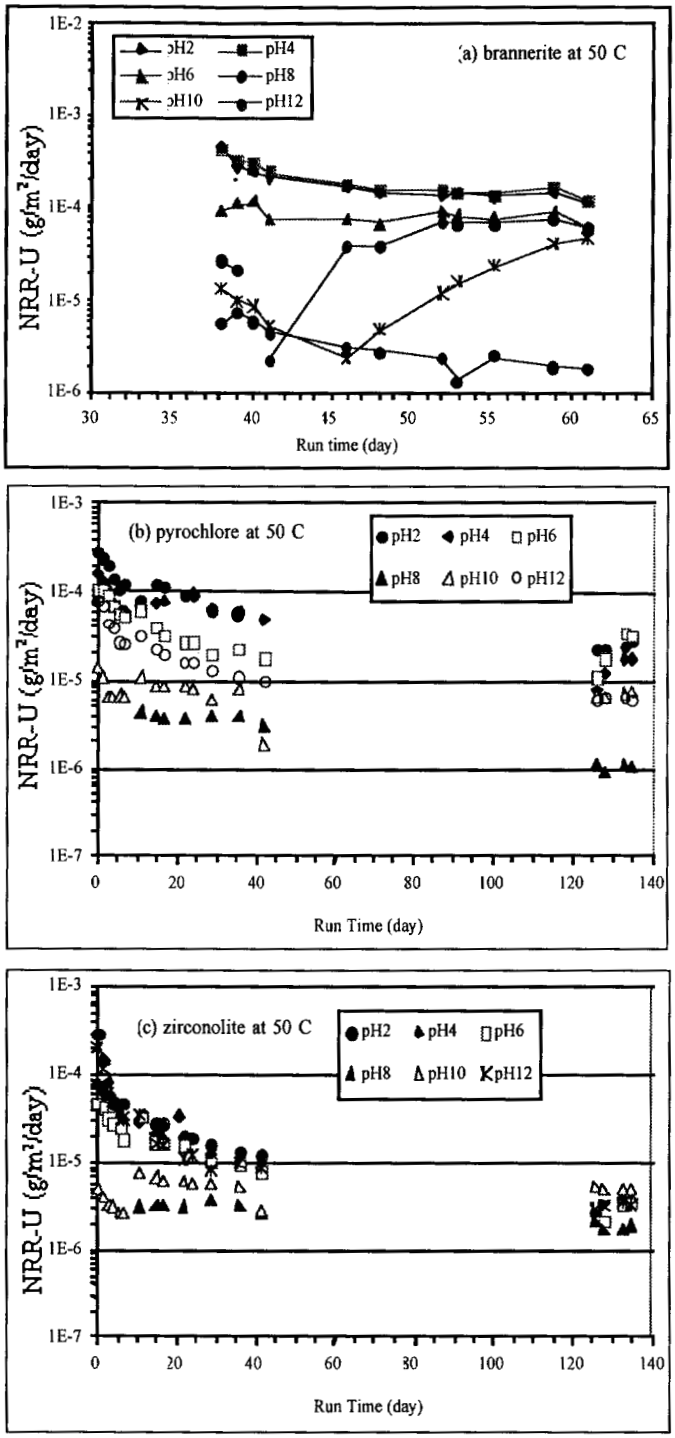

Figure 6. Normalized release rates of uranium from single-phase ceramics at 50° C for (a) brannerite, (b) pyrochlore, and (c) zirconolite.

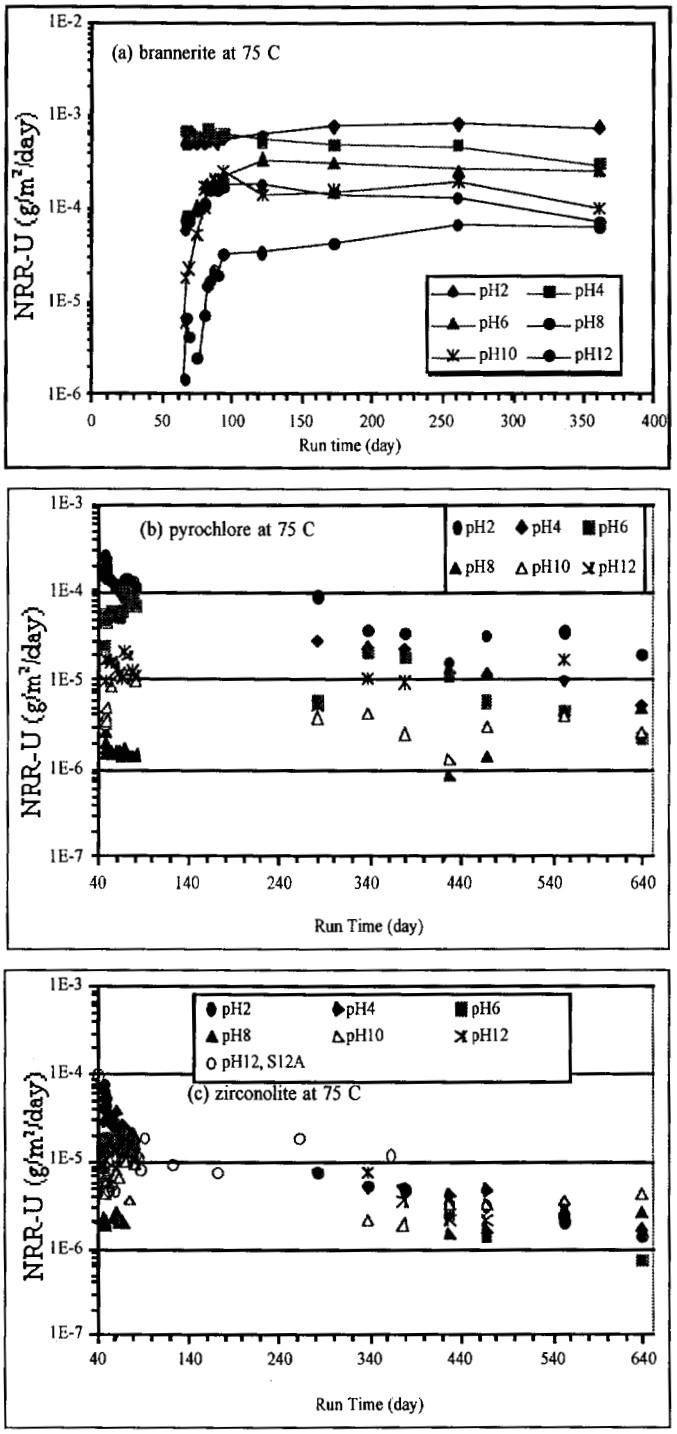

Figure 7. Normalized release rates of uranium from single-phase ceramics at 75° C for (a) brannerite, (b) pyrochlore, and (c) zirconolite.

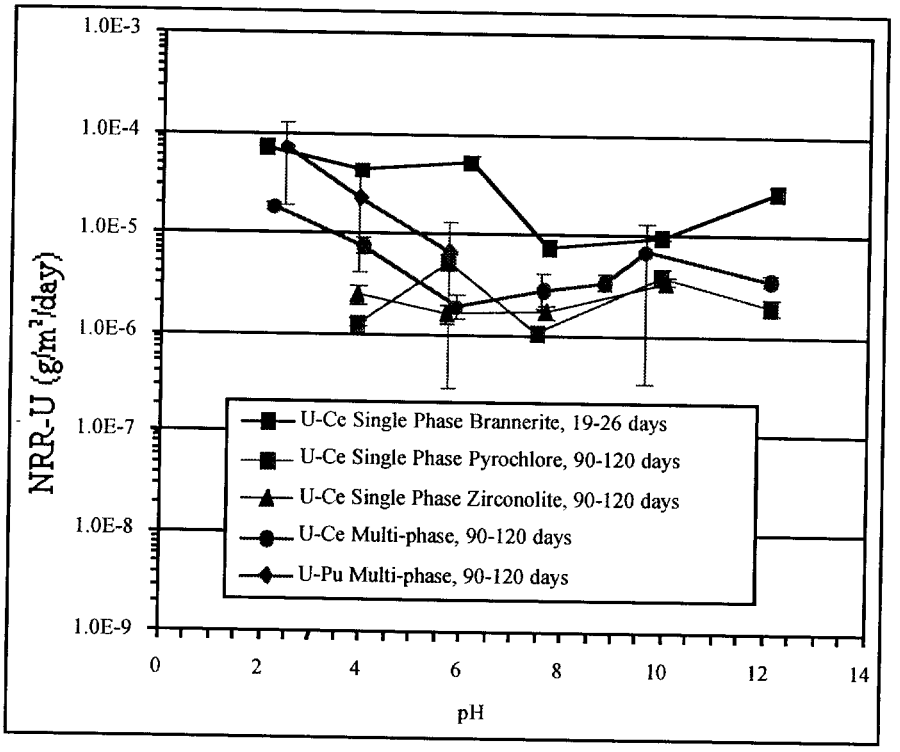

Figure 8. Comparison of dissolution rates of uranium from multi-phase and single phase tests as a function of pH at 25° C.

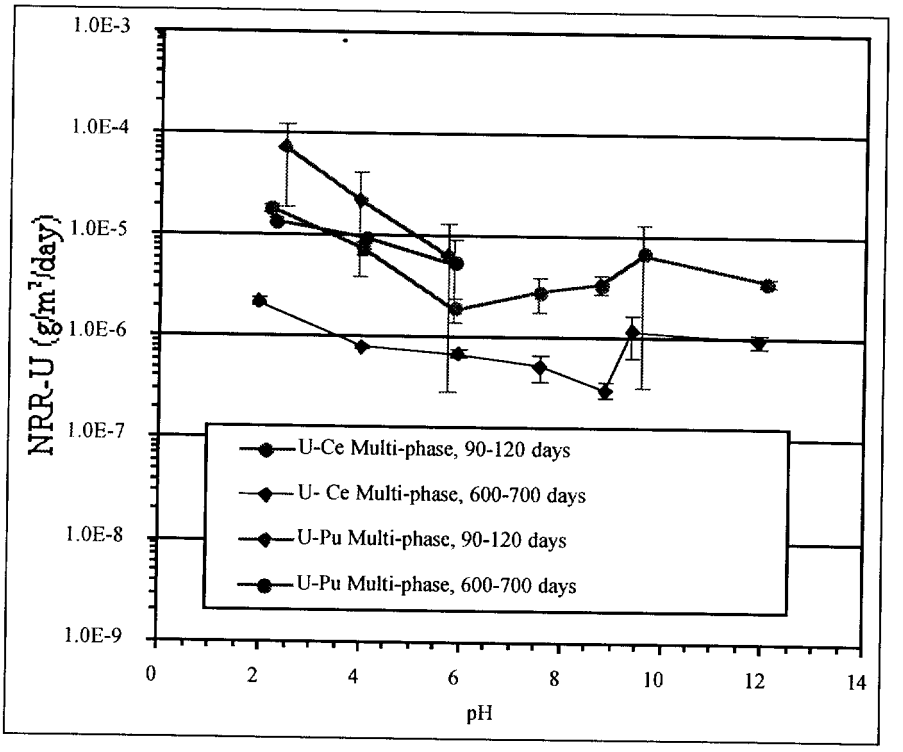

Figure 9. Comparison of dissolution rates of uranium from U-Ce vs. U-Pu ceramics as a function of pH at room temperature.

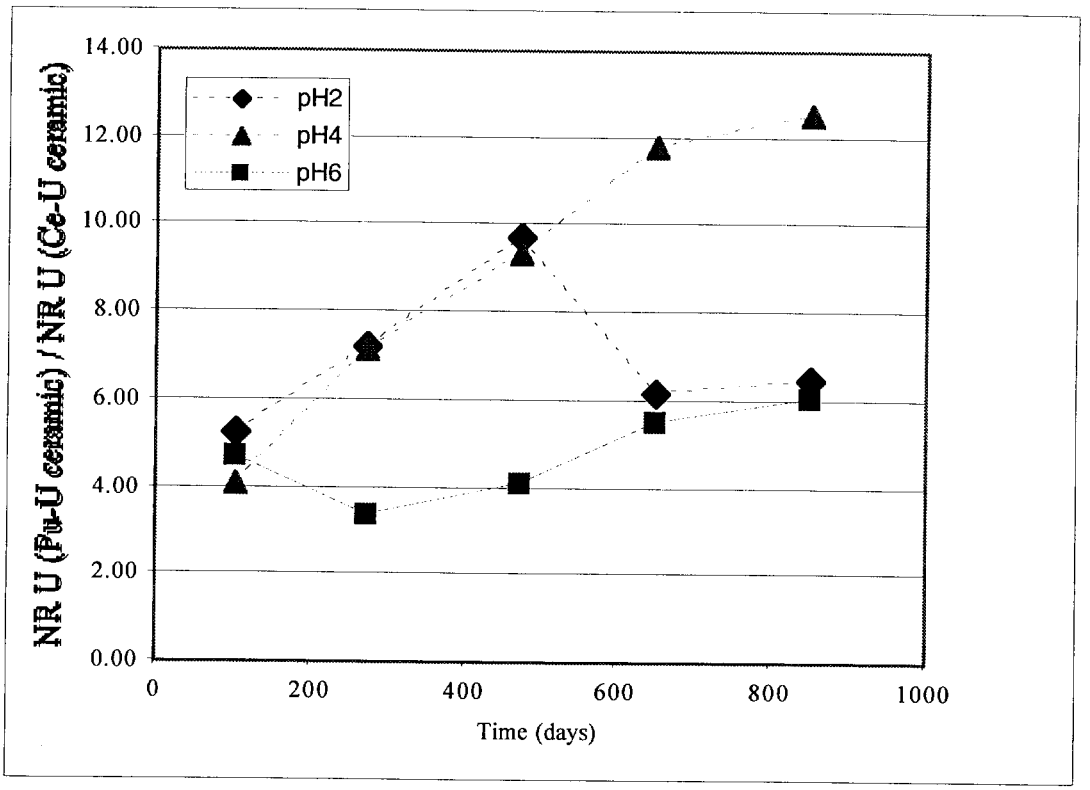

Figure 10. Comparison of uranium release rates from Pu-U and Ce-U ceramics. The ratio of NR of U from the Pu-U ceramic over the NR of U from the Ce-U ceramic is plotted vs. time. At greater times, the relative durability of the Ce-U ceramic increases relative to the Pu-U ceramic, perhaps indicating some deterioration in durability due to radiation damage by Pu in the Pu-U ceramic.

Appendices

The appendices contain all data obtained from the single-pass flow through tests of the ceramic waste forms.

Appendix A. Pu-U Multi-phase Pyrochlore-based Ceramic Waste Form
Appendix B. Ce-U Multi-phase Pyrochlore-based Ceramic Waste Form
Appendix C. Ce-U Single Phase Zirconolite
Appendix D. Ce-U Single Phase Pyrochlore
Appendix E. Ce-U Single Phase Brannerite

Notes:

1. Surface areas measured using nitrogen BET. Surface area of Pu-U ceramic material was estimated based on particle size and comparison with BET measurements of Ce-U material.
2. "Mass" refers to mass of ceramic powder used in test.
3. "Surf Area" is calculated surface area based on starting mass, BET measurement, and a correction term that takes into account surface area loss over duration of experiment as particles decrease in size. The calculation assumes smooth spherical particles and is based on uranium normalized release rates.
4. "NR" refers to normalized release rates for the element as defined on page 4 of text.
5. "% loss" is calculated mass loss assuming stoichiometric dissolution and is based on uranium release. Uranium is generally the fastest released element. The % loss is therefore a conservative upper limit on total mass released.
6. "Calc thickness" is the calculated thickness of material dissolved from the particle surface. As with '% loss', it is calculated from the normalized release rate of uranium and assumes stoichiometric dissolution. As such it provides an estimate of the total amount of particle dissolution. "Calc thickness" can also be used as an estimate of the surface leached layer thickness assuming uranium is preferentially released from the surface layer and the titanate framework remains. The more relevant interpretation depends on the pH of the test. At low pH values where release is nearly congruent, 'Calc thickness' corresponds to the thickness of material that has been dissolved from the surface. At neutral pH values where release is incongruent (uranium is released more quickly than Ti, Hf and other elements), it is a better estimate for leached layer thickness.

plot of relative rates of Ce-U ceramic vs. Pu-U ceramic at pH 2, 4, and 6 (to see if rad damage is increasing the dissolution rate of the pU ceramic relative to the Ce ceramic)

NR values of U release

		pH 2	pH 4	pH 6
	days			
Pu-U ceramic	90-120	9.89E-05	3.20E-05	9.04E-06
	250-300	7.47E-05	1.88E-05	6.77E-06
	450-500	2.91E-05	1.10E-05	2.82E-06
	600-700	1.35E-05	9.27E-06	5.22E-06
	800-900	1.04E-05	8.87E-06	4.31E-06
	days			
Ce-U ceramic	90-120	1.88E-05	7.80E-06	1.92E-06
	250-300	1.04E-05	2.62E-06	2.02E-06
	450-500	2.99E-06	1.18E-06	6.94E-07
	600-700	2.19E-06	7.87E-07	9.47E-07
	800-900	1.60E-06	7.08E-07	7.11E-07

Ratio Pu/Ce	days	2	4	6	days
	90-120	5.26	4.11	4.71	105
	250-300	7.22	7.16	3.35	275
	450-500	9.75	9.36	4.07	475
	600-700	6.15	11.77	5.52	650
	800-900	6.51	12.52	6.06	850